

Dynamics of a polymer test chain in a glass forming matrix: the Hartree approximation

M. Rehkopf^(a), V.G. Rostiashvili^(a,b) and T.A. Vilgis^(a)

^(a) *Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany*

^(b) *Institute of Chemical Physics, Russian Academy of Science, 142432, Chernogolovka,*

Moscow region, Russia

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Abstract

We consider the Langevin dynamics of a Gaussian test polymer chain coupled with a surrounding matrix which can undergo the glass transition. The Martin-Siggia-Rose generating functional method and the nonperturbative Hartree approximation are used to derive the generalized Rouse equation for the test chain. It is shown that the interaction of the test chain with the surrounding matrix renormalizes the bare friction and the spring constants of the test chain in such a way that the memory function as well as the bending dependent elastic modulus appear. We find that below the glass transition temperature T_G of the matrix the Rouse modes of the test chain can be frozen and moreover the freezing temperatures (or the ergodicity-nonergodicity transition temperature) $T_c(p)$ depends from the Rouse mode index p .

I. INTRODUCTION

It is wellknown that for relatively short polymer chains the standard Rouse model can describe the dynamics of a melt reasonably well [1,2]. On the contrary, for chain length N exceeding a critical length, the entanglement length N_e , the behavior is usually described by the reptation model [1]. Here we restrict ourselves to chain lengths $N < N_e$, i.e. the entangled polymer dynamics will be beyond of our consideration.

The reason why in a dense melt the Rouse model provides so well dynamical description for short chains is connected with a screening of the long-range hydrodynamic as well as the excluded volume interactions. As a result the fluctuations of the chain variables are Gaussian. But there are further essential questions: How does the bare monomeric friction coefficient ξ_0 and the entropic elastic modulus ε (which are simple input parameters of the standard Rouse model) change due to the interactions of the test chain and the surrounding matrix? Why does such a simple model work so well for describing short chain melts? Obviously, the corresponding answers cannot be given by the Rouse model, which describes only the dynamics of connected Gaussian springs without further interactions.

On the other hand, at relatively low temperatures close to the glass transition of the surrounding matrix the deviations from the standard Rouse behavior will be definitely more pronounced. For example, Monte Carlo (MC) studies of the bond fluctuation model at low temperatures (but still above the temperature region where possibly the glass transition mode coupling theory [3] applies) show that the Rouse modes remain well-defined eigenmodes of the polymer chains and the chains

retain their Gaussian properties [4]. Nevertheless, the relaxation of the Rouse modes displays a stretched exponential behavior rather than a pure exponential. It could even be expected that at temperatures below the glass transition temperature of the matrix T_G the Rouse modes are frozen out. In these temperature regimes the interactions between monomers take a significant role and determine the physical picture of the dynamics as will be shown below.

The generalized Rouse equation (GRE), which can be used for the investigation of the problems mentioned above, has been derived by using projection formalism methods and mode coupling approximations (MCA) [5–7]. As a result of projection operator formalism the time evolution of the test chain is expressed in terms of a frequency matrix, which is local in time, and a memory function contribution due to the inter-chain forces exerted on the test chain segments. With the assumption that the frequency matrix term has the same form as in the standard Rouse model (linear elasticity with the entropic modulus $\varepsilon = 3k_bT/l^2$) all influence of the matrix chains reduce to the memory function contribution [5–7].

The projection operator methods appears to be exact but rather formal, and to derive explicit results further approximations have to be made, which can be hardly controlled often. Therefore it is instructive to use another alternative theoretical method to derive the GRE. Recently, a non-perturbative variational method which is equivalent to a selfconsistent Hartree approximation was used for the investigation of the dynamics of manifolds [8] and sine-Gordon model [9] in a random media. As a starting point the authors employed the standard Martin-Siggia-Rose (MSR) functional integral technique [10,11]. Here we follow this approach to derive a GRE and study the dynamics of a test polymer chain in a glass forming matrix.

The paper is organized as follows. In section 2, we give a general MSR-functional integral formulation for a test chain in a polymer (or non-polymer) matrix. Under the assumption that the fluctuations of the test chain are Gaussian the Hartree-type approximation is applied and a GRE is finally derived. The case when the fluctuation dissipation theorem (FDT) and the time homogeneity are violated is also shortly considered. In section 3 on the basis of the GRE some static and dynamical properties of the test chain are discussed. In particular the theory of the test chain ergodicity breaking (freezing) in a glassy matrix is formulated. Section 4 gives some summary and general discussion. The appendices are devoted to some technical details of the Hartree-type approximation.

II. GENERALIZED ROUSE EQUATION (GRE)

A. MSR-functional integral approach

Let us consider a polymer test chain with configurations characterized by the vector function $\mathbf{R}(s, t)$ with s numerating the segments of the chain, $0 \leq s \leq N$, and time t . The test polymer chain moves in the melt of the other polymers (matrix) which positions in space are specified by the vector functions $\mathbf{r}^{(p)}(s, t)$, where the index $p = 1, 2, \dots, M$ numerates the different chains of the matrix. The test chain is expected to have Gaussian statistics due to the screening of the self-interactions in a melt [1]. We consider the simultaneous dynamical evolution of the $\mathbf{R}(s, t)$ and $\mathbf{r}^{(p)}(s, t)$ variables assuming that the interaction between matrix and test chain is weak.

The Langevin equations for the full set of variables $\{\mathbf{R}(s, t), \mathbf{r}^{(1)}(s, t), \dots, \mathbf{r}^{(M)}(s, t)\}$

has the form

$$\begin{aligned} \xi_0 \frac{\partial}{\partial t} R_j(s, t) - \varepsilon \frac{\partial^2}{\partial s^2} R_j(s, t) + \frac{\delta}{\delta R_j(s, t)} \sum_{p=1}^M \int_0^N ds' V(\mathbf{R}(s, t) - \mathbf{r}^{(p)}(s', t)) \\ = f_j(s, t) \end{aligned} \quad (1)$$

$$\begin{aligned} \xi_0 \frac{\partial}{\partial t} r_j^{(p)}(s, t) - \varepsilon \frac{\partial^2}{\partial s^2} r_j^{(p)}(s, t) + \frac{\delta}{\delta r_j^{(p)}(s, t)} \sum_{m=1}^M \int_0^N ds' \tilde{V}(\mathbf{r}^{(p)}(s, t) - \mathbf{r}^{(m)}(s', t)) \\ + \frac{\delta}{\delta r_j^{(p)}(s, t)} \sum_{m=1}^M \int_0^N ds' V(\mathbf{r}^{(p)} - \mathbf{R}(s', t)) = \tilde{f}_j(s, t) \end{aligned} \quad (2)$$

where ξ_0 denotes the bare friction coefficient, $\varepsilon = 3T/l^2$ the bare elastic modulus with the length of a Kuhn segment denoted by l , $V(\dots)$ and $\tilde{V}(\dots)$ are the interaction energies of test chain-matrix and matrix-matrix respectively, and $f_j(s, t)$, $\tilde{f}_j(s, t)$ are the random forces with the correlator

$$\langle f_i(s, t) f_j(s', t') \rangle = \langle \tilde{f}_i(s, t) \tilde{f}_j(s', t') \rangle = 2T \xi_0 \delta_{ij} \delta(s - s') \delta(t - t'). \quad (3)$$

After using the standard MSR-functional integral representation [10] for the system (1-3), the generating functional (GF) takes the form

$$\begin{aligned} Z \{ \dots \} = \int DR_j(s, t) D\hat{R}_j(s, t) \int \prod_{p=1}^M Dr_j^{(p)}(s, t) D\hat{r}_j^{(p)}(s, t) \\ \times \exp \left\{ -A_0 [\mathbf{R}(s, t), \hat{\mathbf{R}}(s, t)] - A_1 [\mathbf{r}^{(p)}(s, t), \hat{\mathbf{r}}^{(p)}(s, t)] \right. \\ + \sum_{p=1}^M \int_0^N ds \int_0^N ds' \int dt i \hat{R}_j(s, t) \frac{\delta}{\delta R_j(s, t)} V[\mathbf{R}(s, t) - \mathbf{r}^{(p)}(s', t)] \\ \left. + \sum_{p=1}^M \int_0^N ds \int_0^N ds' \int dt i \hat{r}_j^{(p)}(s', t) \frac{\delta}{\delta r_j^{(p)}(s', t)} V[\mathbf{r}^{(p)}(s', t) - \mathbf{R}(s, t)] \right\} \end{aligned} \quad (4)$$

where the dots represents some source fields which will be specified later and Einstein's summation convention for repeated indices is used. In GF (4) the MSR-action of the free test chain is given by

$$A_0 [\mathbf{R}(s, t), \hat{\mathbf{R}}(s, t)] = - \int_0^N ds \int dt \left\{ i \hat{R}_j(s, t) \left[\xi_0 \frac{\partial}{\partial t} R_j(s, t) - \varepsilon \frac{\partial^2}{\partial s^2} R_j(s, t) \right] + T \xi_0 [i \hat{\mathbf{R}}(s, t)]^2 \right\} . \quad (5)$$

As we will realize later the explicit form of the full action of the medium $A_1 [\mathbf{r}^{(p)}(s, t), \hat{\mathbf{r}}^{(p)}(s, t)]$ plays no role. In principle it could have any form and in particular, for a polymer matrix, the following one

$$\begin{aligned} A_1 [\mathbf{r}^{(p)}(s, t), \hat{\mathbf{r}}^{(p)}(s, t)] = & - \sum_{p=1}^M \int_0^N ds \int dt i \hat{r}_j^{(p)}(s, t) \left[\xi_0 \frac{\partial}{\partial t} r_j^{(p)}(s, t) - \varepsilon \frac{\partial^2}{\partial s^2} r_j^{(p)}(s, t) \right] \\ & - \sum_{p=1}^M \int_0^N ds \int dt i \hat{r}_j^{(p)}(s, t) \frac{\delta}{\delta r_j^{(p)}(s, t)} \sum_{m=1}^M \int ds' \tilde{V} [\hat{\mathbf{r}}^{(p)}(s, t) - \hat{\mathbf{r}}^{(m)}(s', t)] \\ & + \sum_{p=1}^M \int_0^N ds \int dt T \xi_0 [i \hat{r}_j(s, t)]^2 \end{aligned} \quad (6)$$

In order to obtain an equation of motion for the test chain one should integrate over the matrix variables $\mathbf{r}^{(p)}(s, t)$ first. For this end it is reasonable to represent GF (4) as

$$\begin{aligned} Z \{ \dots \} = & \int D R_j(s, t) D \hat{R}_j(s, t) \\ & \times \exp \left\{ - \Xi [R_j(s, t), \hat{R}_j(s, t)] - A_0 [\mathbf{R}(s, t), \hat{\mathbf{R}}(s, t)] \right\} \end{aligned} \quad (7)$$

where the influence functional Ξ is given by

$$\begin{aligned} \Xi [\mathbf{R}, \hat{\mathbf{R}}] = & - \ln \int \prod_{p=1}^M D \mathbf{r}^{(p)}(s, t) D \hat{\mathbf{r}}^{(p)}(s, t) \times \\ & \times \exp \left\{ - A_1 [\mathbf{r}^{(p)}, \hat{\mathbf{r}}^{(p)}] \right. \\ & + \sum_{p=1}^M \int_0^N ds \int_0^N ds' \int dt i \hat{R}_j(s, t) \frac{\delta}{\delta R_j(s, t)} V [\mathbf{R}(s, t) - \mathbf{r}^{(p)}(s', t)] \\ & \left. + \sum_{p=1}^M \int_0^N ds \int_0^N ds' \int dt i \hat{r}_j^{(p)}(s', t) \frac{\delta}{\delta r_j(s', t)} V [\mathbf{r}^{(p)}(s', t) - \mathbf{R}(s, t)] \right\}. \end{aligned} \quad (8)$$

In the spirit of the mode coupling approximation (MCA) [3,6] the force between the test chain and the matrix should be expressed as a bilinear product of the two

subsystems densities. In order to assure this we expand the influence functional (8) with respect to the forces $F_j = -\nabla_j V$ between the test chain and the matrix up to the second order. This leads to

$$\begin{aligned}
\Xi[\mathbf{R}, \hat{\mathbf{R}}] = & -\ln \int \prod_{p=1}^M D\mathbf{r}^{(p)}(s, t) D\hat{\mathbf{r}}^{(p)}(s, t) \left\{ \exp \{ -A_1[\mathbf{r}^p, \hat{\mathbf{r}}^p] \} \right. \\
& + \frac{1}{2!} \int d^3r d^3r' \int ds \int ds' \int dt i\hat{R}_j(s, t) \frac{\delta}{\delta R_j(s, t)} V[\mathbf{R}(s, t) - \mathbf{r}] \\
& \quad \times \int dt' i\hat{R}_l(s', t') \frac{\delta}{\delta R_l(s', t')} V[\mathbf{R}(s', t') - \mathbf{r}'] \langle \rho(\mathbf{r}, t) \rho(\mathbf{r}', t') \rangle_1 \\
& + \frac{1}{2!} \int d^3r d^3r' \int ds \int ds' \int dt \int dt' V[\mathbf{r} - \mathbf{R}(s, t)] V[\mathbf{r}' - \mathbf{R}(s', t')] \\
& \quad \times \nabla_l \nabla'_j \langle \Pi_l(\mathbf{r}, t) \Pi_j(\mathbf{r}', t') \rangle_1 \\
& - \frac{1}{2!} \int d^3r d^3r' \int ds \int ds' \int dt \int_{-\infty}^t dt' i\hat{R}_j(s, t) \frac{\delta}{\delta R_j(s, t)} V[\mathbf{R}(s, t) - \mathbf{r}] \\
& \quad \times V[\mathbf{r}' - \mathbf{R}(s', t')] \nabla'_l \langle \rho(\mathbf{r}, t) \Pi_l(\mathbf{r}', t') \rangle_1 \\
& + (t \Leftrightarrow t') + \mathcal{O}(F^3) \left. \right\} \tag{9}
\end{aligned}$$

where the matrix density

$$\rho(\mathbf{r}, t) = \sum_{p=1}^M \int_0^N ds \delta(\mathbf{r} - \mathbf{r}^{(p)}(s, t)) \tag{10}$$

and the response field density

$$\Pi_j(\mathbf{r}, t) = \sum_{p=1}^M \int_0^N ds i\hat{\mathbf{r}}_j^{(p)}(s, t) \delta(\mathbf{r} - \mathbf{r}^{(p)}(s, t)) \tag{11}$$

were introduced and $\langle \dots \rangle_1$ denotes cumulant averaging over the full MSR-action $A_1[\mathbf{r}, \hat{\mathbf{r}}]$ of the matrix. In eq. (9) the term $(t' \Leftrightarrow t)$ is the same like the previous one but with permuted time arguments. The terms which are linear with respect to F_j vanishes because of the homogeneity of the system. In the Appendix A we show that because of causality the correlator $\langle \Pi_l(\mathbf{r}, t) \Pi_j(\mathbf{r}', t') \rangle_1$ equals zero [10–12]. Taking this into account and performing the spatial Fourier transformation the expression for GF (7) takes the form

$$\begin{aligned}
Z \{ \cdots \} = & \int DR_j(s, t) D\hat{R}_j(s, t) \exp \left\{ -A_0 [\mathbf{R}(s, t), \hat{\mathbf{R}}(s, t)] \right. \\
& + \frac{1}{2} \int ds ds' \int dt dt' i\hat{R}_j(s, t) \int \frac{d^3 k}{(2\pi)^3} k_j k_l |V(k)|^2 S(\mathbf{k}, t - t') \\
& \quad \times \exp \{ i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')] \} i\hat{R}_l(s', t') \\
& + \int ds ds' \int dt dt' i\hat{R}_j(s, t) \int \frac{d^3 k}{(2\pi)^3} k_j k_l |V(k)|^2 P_l(\mathbf{k}, t - t') \\
& \quad \left. \times \exp \{ i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')] \} \right\} \quad (12)
\end{aligned}$$

where the correlation function

$$S(\mathbf{k}, t) \equiv \langle \rho(\mathbf{k}, t) \rho(-\mathbf{k}, 0) \rangle_1 \quad (13)$$

and the response function

$$P_l(\mathbf{k}, t) \equiv \langle \rho(\mathbf{k}, t) \Pi_l(-\mathbf{k}, 0) \rangle_1 \quad (14)$$

of the matrix are naturally defined. Going beyond the LRT-approximation would bring us multi-point correlation and response functions.

We should stress that in contrast to the matrix with a quenched disorder which was considered in [8,9] in our case the matrix has its own intrinsic dynamical evolution which is considered as given. For example, for the glass forming matrix, which is our prime interest here, the correlation and response functions are assumed to be governed by the Götze mode-coupling equations [3].

B. The Hartree approximation

The Hartree approximation (which is actually equivalent to the Feynman variational principle) was recently used for the replica field theory of random manifolds [13] as well as for the dynamics of manifolds [8] and sine-Gordon model [9] in a random media.

In the Hartree approximation the real MSR-action is replaced by a Gaussian action in such a way that all terms which include more than two fields $R_j(s, t)$ or/and $\hat{R}_j(s, t)$ are written in all possible ways as products of pairs of $R_j(s, t)$ or/and $\hat{R}_j(s, t)$, coupled to selfconsistent averages of the remaining fields. As a result the Hartree-action is a Gaussian functional with coefficients, which could be represented in terms of correlation and response functions. After these straightforward calculations (details can be found in the Appendix B) the GF (12) takes the form

$$\begin{aligned}
Z \{ \cdots \} = & \int DR_j(s, t) D\hat{R}_j(s, t) \exp \left\{ -A_0 [\mathbf{R}(s, t), \hat{\mathbf{R}}(s, t)] \right. \\
& + \int_0^N ds ds' \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' i\hat{R}_j(s, t) R_j(s', t') \lambda(s, s'; t, t') \\
& - \int_0^N ds ds' \int_{-\infty}^{\infty} dt i\hat{R}_j(s, t) R_j(s, t) \int_{-\infty}^t dt' \lambda(s, s'; t, t') \\
& \left. + \frac{1}{2} \int_0^N ds ds' \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' i\hat{R}_j(s, t) i\hat{R}_j(s', t') \chi(s, s'; t, t') \right\} \quad (15)
\end{aligned}$$

where

$$\begin{aligned}
\lambda(s, s'; t, t') = & \frac{1}{3} G(s, s'; t, t') \int \frac{d^3 k}{(2\pi)^3} k^4 |V(k)|^2 F(\mathbf{k}; s, s'; t, t') S(\mathbf{k}; t, t') \\
& - \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 F(\mathbf{k}; s, s'; t, t') P(\mathbf{k}; t, t') \quad (16)
\end{aligned}$$

and

$$\chi(s, s'; t, t') = \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 F(\mathbf{k}; s, s'; t, t') S(\mathbf{k}; t, t') \quad (17)$$

In eq. (16,17) the response function

$$G(s, s'; t, t') = \langle i\hat{\mathbf{R}}(s', t') \mathbf{R}(s, t) \rangle, \quad (18)$$

the density correlator

$$F(\mathbf{k}; s, s'; t, t') = \exp \left\{ -\frac{k^2}{3} Q(s, s'; t, t') \right\} \quad (19)$$

with

$$\begin{aligned} Q(s, s'; t, t') &\equiv \langle \mathbf{R}(s, t) \mathbf{R}(s, t) \rangle - \langle \mathbf{R}(s, t) \mathbf{R}(s', t') \rangle \\ &= C(s, s; t, t) - C(s, s'; t, t') \end{aligned} \quad (20)$$

and the longitudinal part of the matrix response function

$$P(\mathbf{k}; t, t') = ik_j P_j(\mathbf{k}; t, t') \quad (21)$$

are defined. The pointed brackets denote the selfconsistent averaging with the Hartree-type GF (15).

Up to now we considered the general off-equilibrium dynamics with the only restriction of causality [10–12]. We now assume that for very large time moments t and t' , where the difference $t - t'$ is finite so that $\frac{t-t'}{t} \rightarrow 0$, time homogeneity and the fluctuation-dissipation theorem (FDT) holds. This implies

$$G(s, s'; t, t') = G(s, s'; t - t') = \beta \frac{\partial}{\partial t'} Q(s, s'; t - t') \quad , \quad t > t' \quad (22)$$

$$P(\mathbf{k}; t, t') = P(\mathbf{k}; t - t') = \beta \frac{\partial}{\partial t'} S(\mathbf{k}; t - t') \quad , \quad t > t' \quad (23)$$

where $\beta \equiv 1/T$. By using this in eq. (15) and after integration by parts in the integrals over t' the GF in Hartree approximation takes the form

$$\begin{aligned} Z \{ \dots \} &= \int D R_j(s, t) D \hat{R}_j(s, t) \\ &\times \exp \left\{ \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' i \hat{R}_j(s, t) \left[\xi_0 \delta(t - t') \delta(s - s') + \right. \right. \\ &\quad \left. \left. + \Theta(t - t') \beta \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 F(\mathbf{k}; s, s'; t - t') S(\mathbf{k}; t - t') \right] \frac{\partial}{\partial t'} R_j(s', t') \right. \\ &\quad \left. - \int_0^N ds ds' \int_{-\infty}^{\infty} dt i \hat{R}_j(s, t) \left[\varepsilon \delta(s - s') \frac{\partial^2}{\partial s^2} + \beta \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 S_{st}(\mathbf{k}) \right. \right. \\ &\quad \left. \left. \times \left[F_{st}(\mathbf{k}; s, s') - \delta(s - s') \int_0^N ds'' F_{st}(\mathbf{k}; s, s'') \right] \right] R_j(s', t) \right\} \end{aligned}$$

$$\begin{aligned}
& + T \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' \left[\xi_0 \delta(t - t') \delta(s - s') + \Theta(t - t') \beta \right. \\
& \left. \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 F(\mathbf{k}; s, s'; t - t') S(\mathbf{k}; t - t') \right] i\hat{R}_j(s, t) i\hat{R}_j(s', t') \quad (24)
\end{aligned}$$

where the subscript "st" indicates the static correlation functions. This generating functional immediately leads to the following generalized Rouse equation (GRE)

$$\begin{aligned}
& \xi_0 \frac{\partial}{\partial t} R_j(s, t) + \int_0^N ds' \int_{-\infty}^t dt' \Gamma(s, s'; t - t') \frac{\partial}{\partial t'} R_j(s', t') \\
& - \int_0^N ds' \Omega(s, s') R_j(s', t) = \mathcal{F}_j(s, t), \quad (25)
\end{aligned}$$

where the memory function

$$\Gamma(s, s'; t - t') = \beta \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 F(\mathbf{k}; s, s'; t - t') S(\mathbf{k}; t - t') \quad (26)$$

and the effective elastic susceptibility

$$\begin{aligned}
& \Omega(s, s') = \varepsilon \delta(s - s') \frac{\partial^2}{\partial s^2} + \beta \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 S_{st}(\mathbf{k}) \times \\
& \times \left[F_{st}(\mathbf{k}; s, s') - \delta(s - s') \int_0^N ds'' F_{st}(\mathbf{k}; s, s'') \right] \quad (27)
\end{aligned}$$

are defined. The correlation function of the random force \mathcal{F}_j is given by

$$\langle \mathcal{F}_i(s, t) \mathcal{F}_j(s', t') \rangle = 2T \delta_{ij} \left[\xi_0 \delta(s - s') \delta(t - t') + \Theta(t - t') \Gamma(s, s'; t - t') \right] \quad (28)$$

As a result we have obtained basically the same GRE as in the papers [5–7] but with one additional elastic term. This term (see the 2-nd term in eq. (27)) is mainly inversely proportional to the temperature and is, in contrast to the first term, of an energetic nature. The two factors of $kV(k)$ quantify the forces exerted by a pair of surrounding segments on the test chain segments s and s' , whereas the $S_{st}(\mathbf{k})$ and $F_{st}(\mathbf{k}; s, s')$ factors quantify the static correlations between the segments of surrounding and test chain segments, respectively. In [5–7] only the entropic

elastic part was taken into account. The memory function (26) has the same form as in [5–7] and the relationship (28) is assured as soon as the FDT (22) and (23) is fulfilled.

C. Generalized Rouse equations for the off-equilibrium dynamics

In this subsection we give GRE's for the more general case when the time homogeneity (stationarity) and the FDT do not hold [14].

By employing the standard way [8] one can derive two coupled equations of motion for correlators $C(s, s'; t, t')$ and response functions $G(s, s'; t, t')$

$$\begin{aligned} & \left[\xi_0 \frac{\partial}{\partial t} - \varepsilon \frac{\partial^2}{\partial s^2} - \int_0^N ds'' \int_{-\infty}^t dt'' \lambda(s, s''; t, t'') \right] G(s, s'; t, t') \\ & + \int_0^N ds'' \int_{-t'}^t dt'' \lambda(s, s''; t, t'') G(s'', s'; t'', t') = \delta(s - s') \delta(t - t') \end{aligned} \quad (29)$$

$$\begin{aligned} & \left[\xi_0 \frac{\partial}{\partial t} - \varepsilon \frac{\partial^2}{\partial s^2} - \int_0^N ds'' \int_{-\infty}^t dt'' \lambda(s, s''; t, t'') \right] C(s, s'; t, t') \\ & + \int_0^N ds'' \int_{-\infty}^t dt'' \lambda(s, s''; t, t'') C(s'', s'; t'', t') \\ & + \int_0^N ds'' \int_{-\infty}^t dt'' \chi(s, s''; t, t'') G(s', s''; t', t'') = 2T\xi_0 G(s', s; t', t) \end{aligned} \quad (30)$$

with the initial conditions

$$\begin{aligned} \xi_0 G(s, s'; t = t' + 0^+) &= \delta(s - s') \\ G(s, s'; t = t') &= 0, \quad t \leq t' \end{aligned} \quad (31)$$

and

$$C(s, s'; t = t') = \langle \mathbf{R}(s, t) \mathbf{R}(s', t) \rangle \quad (32)$$

In the stationary case all correlators and response functions in eq. (29-32) only depend from the differences of time moments, $t - t'$. If we assume again that FDT

(22) and (23) holds, then from eq. (30) after performing the integrations by parts (in the integrals over t'') one arrive at the GRE for $t > 0$

$$\begin{aligned} \xi_0 \frac{\partial}{\partial t} C(s, s'; t) + \int_{-\infty}^t dt' \int_0^N ds'' \Gamma(s, s''; t - t') \frac{\partial}{\partial t'} C(s'', s'; t') \\ - \int_0^N ds'' \Omega(s, s'') C(s'', s'; t) = 0. \end{aligned} \quad (33)$$

Of course, eq. (33) could be obtained immediately from eq. (25) by multiplying both sides with $R_j(s', 0)$, averaging and taking into account that because of causality $\langle \mathcal{F}(s, t) \mathbf{R}(s', 0) \rangle = 0$ at $t > 0$. We will use the GRE eq.(33), where the functions Γ and Ω are given by eqs. (26, 27), in the next section for the investigation of the test chain ergodicity breaking (freezing).

III. SOME STATICAL AND DYNAMICAL PROPERTIES OF THE TEST CHAIN

The new features of the GRE (33) relative to the standard Rouse equation are that it contains the integral convolution with respect to the s -variable in the frictional term as well as in the elastic term. The frictional term is also non-local in time. All these things together should change the statical and dynamical behaviour of the Gaussian test chain in comparison to the ideal chain.

We also should stress that the GRE is substantially nonlinear because the memory function (26) depends from the test chain correlator $C(s, s'; t)$ in such a way that a positive feedback obviously exists. That is the reason why one could expect that eq. (33) shows an ergodicity breaking in the spirit of Götze's glass transition theory [3].

As usual it is convenient to introduce the standard Rouse mode variables [1]:

$$\mathbf{X}(p, t) = \frac{1}{N} \int_0^N ds \mathbf{R}(s, t) \cos\left(\frac{p\pi s}{N}\right) \quad (34)$$

with the inverse transformation

$$\mathbf{R}(s, t) = \mathbf{X}(p=0, t) + 2 \sum_{p=1}^{\infty} \mathbf{X}(p, t) \cos\left(\frac{p\pi s}{N}\right). \quad (35)$$

In general one also needs a 2-dimensional Rouse transformation

$$\Gamma(p, q; t) = \frac{1}{N^2} \int_0^N ds' \int_0^N ds'' \Gamma(s', s''; t) \cos\left(\frac{p\pi s'}{N}\right) \cos\left(\frac{q\pi s''}{N}\right) \quad (36)$$

where functions like $\Gamma(s', s'')$ should be treated like $N \times N$ -matrices. For example the density correlator (19) should be considered as an exponential function from a $N \times N$ -matrix $Q(s', s'')$ and the series expansion holds :

$$\begin{aligned} F(s, s') &= 1 - \frac{k^2}{3} Q(s, s') + \frac{1}{2} \left(\frac{k^2}{3}\right)^2 \int_0^N ds'' Q(s, s'') Q(s'', s') \\ &\quad - \frac{1}{3!} \left(\frac{k^2}{3}\right)^3 \int_0^N ds'' \int_0^N ds''' Q(s, s'') Q(s'', s''') Q(s''', s') + \dots \end{aligned} \quad (37)$$

We also assume that matrices in the Rouse mode representation are nearby diagonal

$$\Gamma(p, q) = \delta_{p,q} \Gamma(p) \quad (38)$$

$$Q(p, q) = \delta_{p,q} Q(p) \quad (39)$$

$$\Omega(p, q) = \delta_{p,q} \Omega(p) \quad (40)$$

for any p and q not equal zero [1].

Then as a result of Rouse mode transformation the GRE for the Rouse mode time correlation function, $C(p, t) \equiv \langle \mathbf{X}(p, t) \mathbf{X}(p, 0) \rangle$, takes the form (for $p \neq 0$)

$$\xi_0 \frac{d}{dt} C(p, t) + \int_0^t dt' \Gamma(p, t-t') \frac{\partial}{\partial t'} C(p, t') + \Omega(p) C(p, t) = 0 \quad (41)$$

where

$$\Gamma(p, t) = \beta \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 \left\{ \exp \left[\frac{k^2}{3} N C(p, t) \right] - 1 \right\} S(\mathbf{k}, t) \quad (42)$$

and

$$\Omega(p) = \varepsilon \left(\frac{p\pi}{N} \right)^2 - \beta N \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 S_{st}(\mathbf{k}) [F_{st}(\mathbf{k}; p) - F_{st}(\mathbf{k}; p = 0)] \quad (43)$$

For $p = 0$ the GRE describes the dynamics of the centre of mass

$$\mathbf{R}_{c.m}(t) \equiv \mathbf{X}(p = 0, t) = \frac{1}{N} \int_0^N ds \mathbf{R}(s, t) \quad (44)$$

and has the following form

$$\begin{aligned} \xi_0 \frac{d}{dt} \mathbf{R}_{c.m}(t) + \beta \int_0^t dt' \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 F(\mathbf{k}; p = 0, q = 0, t - t') \\ \times S(\mathbf{k}, t - t') \frac{d}{dt'} \mathbf{R}_{c.m}(t') = \mathbf{f}_{c.m}(t) \end{aligned} \quad (45)$$

with

$$(f_{c.m})_j(t) \equiv \frac{1}{N} \int_0^N ds \mathcal{F}_j(s, t) \quad (46)$$

and

$$F(\mathbf{k}; p = 0, q = 0; t) = \frac{1}{N^2} \int_0^N ds' \int_0^N ds'' \exp \left\{ -\frac{k^2}{3} Q(s', s''; t) \right\} \quad (47)$$

As a result all Rouse mode variables relax independently. The conclusion that the Rouse modes are still "good eigenmodes" even in the melt is supported by Monte-Carlo [4] and molecular-dynamic [15] simulations.

For cases where the assumption of diagonality [38,39,40] cannot be justified, the Rouse modes do not decouple and one have to go back to eq. (33). In the Rouse mode representation it reads as

$$\xi_0 \frac{d}{dt} C(p, t) + \int_0^t dt' \int dq \Gamma(p, q; t - t') \frac{\partial}{\partial t'} C(q, t') + \int dq \Omega(p, q) C(q, t) = 0 \quad (48)$$

A. Static properties

As we have already discussed in sec.II.B the interaction with the surrounding segments renormalizes the elastic properties of the Rouse chain so that the test chains elastic susceptibility is given by eq. (43). The additional elastic term in GRE leads to the renormalized static normal modes correlator

$$C_{st}(p) = \frac{T}{2N\Omega(p)} \quad (49)$$

Explicit evaluation of the $\Omega(p)$ can be done if we use for the static correlator $F_{st}(\mathbf{k}; p)$ the standard Rouse expression

$$F_{st}(\mathbf{k}; p) = \frac{1}{N} \int_0^N ds \exp\left(-\frac{l^2 k^2 s}{6}\right) \cos\left(\frac{p\pi s}{N}\right). \quad (50)$$

Then the calculation yields for the two limiting cases

$$\Omega(p) = \begin{cases} \left(\frac{p\pi}{N}\right)^2 \left[\varepsilon + \frac{\beta}{2\pi^2} \int_0^{l^{-1}} dk k^4 |V(k)|^2 S_{st}(k) g(k^2 R_g^2)\right] + \mathcal{O}(p^4) & : \frac{p\pi}{N} \ll 1 \quad (50a) \\ \left(\frac{p\pi}{N}\right)^2 \varepsilon + \frac{\beta}{4\pi^2} \int_0^{l^{-1}} dk k^4 |V(k)|^2 S_{st}(k) \left(\frac{6}{l^2 k^2}\right) (1 - e^{-k^2 R_g^2}) & : \frac{p\pi}{N} \simeq 1 \quad (50b) \end{cases}$$

where

$$g(x) = \frac{1}{x^3} \left[2 - (x^2 + 2x + 2)e^{-x}\right], \quad R_g = \frac{Nl^2}{6} \quad (52)$$

and we have chosen l^{-1} as a cutting parameter. It is evident from the previous eqs. (50a, 50b) that at small p

- the elastic modulus gains an energetic component which, in contrast to the entropic part ε , increase with the cooling of the system,
- initially absolutely flexible chains acquires a stiffness because of terms of order p^4 and higher.

At large p the elastic behaviour reduces to the standard Rouse one, as it is expected. In Fig.1 is shown the result of a numerical calculation of the static correlator (49). The Fourier component of the potential is taken, as it is customary e.g. in the theory of neutron scattering [16], in the form of a pseudo potential approximation, $V(k) = \gamma\sigma^3$, where γ and σ have dimensions of molecular energy and distance, respectively. The static structure factor $S_{st}(\mathbf{k})$ is chosen in the form of the Percus-Yevick's simple liquid model [17]. One can see that for $N = 500$ the small Rouse mode index limit (50a) starts at $\frac{p}{N} \leq 3 \cdot 10^{-3}$ whereas the opposit limit (50b) is fullfilled at $\frac{p}{N} \geq 10^{-1}$. Because the correlator $C_{st}(p)$ depends mainly from p/N , for relatively short test chains the high mode index limit (50b) is shifted into the window of calculations (see Fig.1 for $N=20$).

At least qualitatively this deviation from the standard Rouse behaviour have been seen by Kremer and Grest in their MD-simulations (see Fig.3 in [15]).

B. The test chain ergodicity breaking in a glass forming

matrix

First we consider the case $p \neq 0$. In the nonergodic state the Rouse mode correlation functions can be represented as

$$\Psi(p, t) \equiv \frac{C(p, t)}{C_{st}(p)} = \Psi_{reg}(p, t) + g(p) \quad (53)$$

where the non-ergodicity parameter

$$g(p) \equiv \lim_{t \rightarrow \infty} \Psi(p, t) \quad (54)$$

was introduced and $\Psi_{reg}(p, t \rightarrow \infty) = 0$.

For the correlation function of the glassy matrix we can use the standard result of the glass transition theory [3]

$$\phi(\mathbf{k}, t) \equiv \frac{S(\mathbf{k}, t)}{S_{st}(\mathbf{k})} = f^c(\mathbf{k}) + h(\mathbf{k})\Delta^{1/2} \left(\frac{\tau_\Delta}{t} \right)^a \quad (55)$$

where the proximity parameter $\Delta \equiv (T_G - T)/T_G$ is defined and T_G is the temperature of the matrix ergodicity breaking (Götze temperature). In eq. (55) $f^c(\mathbf{k})$ is the non-ergodicity parameter of the matrix, $\tau_\Delta \propto \Delta^{-1/2a}$ is the characteristic time scale, a is the characteristic exponent, $0 < a < 1/2$ and $h(\mathbf{k})$ is some amplitude.

In order to derive the equation for $g(p)$ let us take the limit $t \rightarrow \infty$ in eq. (41) keeping in mind the definitions (54) and (55). Very close to the test chain ergodicity breaking temperature $T_c(p)$, $g(p)$ goes to zero (A-type transition [3]) and we can expand the exponential function in eq. (42) up to the first order with respect to $g(p)$. The solution of the resulting equation has the simple form

$$g(p) = 1 - \frac{6\Omega(p)^2}{\int \frac{d^3k}{(2\pi)^3} k^4 |V(k)|^2 S_{st}(\mathbf{k}) f^c(\mathbf{k})} \quad (56)$$

The critical temperature $T_c(p)$ is determined by the equation

$$g(p, T = T_c) = 0 \quad (57)$$

The numerical solution of eq. (57) is given in Fig.2. It is obviously that if the entropic part of $\Omega(p)$ dominates, the critical temperature is given by

$$T_c(p) \propto \left(\frac{N}{\pi p} \right)^2. \quad (58)$$

Fig.2 really shows that this law (58) is well satisfied due to the fact that the critical temperatures $T_c(p)$ are quite high. But for low temperatures the energetic contribution in $\Omega(p)$ is enhanced which leads to a deviation from this simple $(N/p)^2$ -dependence.

Now we consider the case for $p = 0$. The equation (45) for the velocity of the center of mass

$$\mathbf{v}(t) \equiv \frac{d}{dt} \mathbf{R}_{c.m.}(t) \quad (59)$$

leads to the equation for the velocity correlator

$$\xi_0 \langle v_j(t) v_i(0) \rangle + \int_0^t dt' \Gamma(t-t') \langle v_j(t') v_i(0) \rangle = \langle (f_{c.m})_j(t) v_i(0) \rangle \quad (60)$$

where

$$\Gamma(t) = \beta \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 F(\mathbf{k}; p = q = 0; t) S(\mathbf{k}, t) \quad (61)$$

Because of causality the correlator on the r.h.s. of eq. (60) has the form

$$\langle (f_{c.m})_j(t) v_i(0) \rangle = \begin{cases} 0 & , \quad t > 0 \\ \neq 0 & , \quad t = 0 \end{cases} \quad (62)$$

where, as it comes from eq. (45)

$$v_i(0) = \frac{1}{\xi_0} (f_{c.m})_i(0) \quad (63)$$

Taking into account the definition of $(f_{c.m})_i(t)$ and eq. (28) this yields to the correlator

$$\begin{aligned} \langle (f_{c.m})_j(t) v_i(0) \rangle &= 2T \delta_{ij} \delta(t) \frac{1}{N^2} \int_0^N ds' \int_0^N ds'' \delta(s' - s'') \\ &= \frac{2T}{N} \delta_{ij} \delta(t) \end{aligned} \quad (64)$$

Because of the causality property (61) only the δ -functional term on the r.h.s. of eq. (28) contributes to the correlator (64). Therefore the resulting equation for the self-diffusion coefficient

$$D \equiv \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(t) \mathbf{v}(0) \rangle \quad (65)$$

takes the form

$$D = \frac{T}{N [\xi_0 + \int_0^\infty dt \Gamma(t)]} \quad (66)$$

which was obtained before in [5,6].

One can calculate the second term in the denominator of eq. (66) selfconsistently.

Because now the relevant times $t \gg \tau_{rouse}$ the approximation

$$Q(s', s''; t) = 6Dt + l^2 |s' - s''| + \text{const.} \quad (67)$$

could be used in eq. (45). Then the density correlator (47) is given by

$$F(\mathbf{k}; p = q = 0; t) = \frac{1}{\frac{k^2 l^2}{12} + N^{-1}} \exp(-k^2 Dt) \quad (68)$$

With the use of eqs. (68),(55) and eq. (61) in the limit $D \rightarrow 0$ eq. (66) becomes

$$D = \frac{T}{N \left[\xi_0 + \frac{1}{TD} \int \frac{d^3 k}{(2\pi)^3} \frac{|V(k)|^2 S_{st}(\mathbf{k})}{\frac{k^2 l^2}{12} + N^{-1}} f(\mathbf{k}) \right]} \quad (69)$$

where the denominator is given by static properties only. Similar statements have been suggested already in [18,19] The solution of eq. (69) has the simple form

$$D = D_0 \left(1 - \frac{N}{T^2} \chi \right) \quad (70)$$

where

$$\chi = \int \frac{d^3 k}{(2\pi)^3} \frac{|V(k)|^2 S_{st}(\mathbf{k})}{\frac{k^2 l^2}{12} + N^{-1}} f(\mathbf{k}) \quad (71)$$

Finally, the temperature of the ergodicity breaking (localization) for the mode $p = 0$ of the test chain is

$$T_c(p = 0) = (N\chi)^{1/2} \quad (72)$$

Fig.3 shows the results of numerical calculations of $T_c(p = 0)$ and $T_c(p = 1)$ as functions of N . One can see that in the reasonable range of parameters $T_c(p = 0) > T_c(p = 1)$. As a result one can say that on cooling of a test chain in a glassy matrix the mode $p = 0$ is the first to be freezed. On the subsequent cooling the modes $p = 1, 2, \dots, N$ are freezed successively,

$$T_G > T_c(p = 0) > T_c(p = 1) > T_c(p = 2) > \dots T_c(p = N). \quad (73)$$

It is apparent that the system studied here is a nontrivial polymeric generalization of the model introduced by Sjögren [20]. This model was used for the investigation of the β -peak in the spectrum of glass forming systems [21].

IV. DISCUSSION

In this paper we have derived a GRE for a test polymer chain in a polymer (or non-polymer) matrix which has its own intrinsic dynamics, e.g. the glassy dynamics [3]. We have used here the MSR-functional integral technique which could be considered as an alternative to the projection operator formalism [6]. One of the difficulties in this formalism is the necessity of dealing with the projected dynamic, which is difficult to handle with explicitly. On the contrary in MSR-technique the dynamic of slow variables is well defined and several approximations which one have to employ could be justified.

In the interaction of the test chain with the surrounding matrix only two-point correlation and response functions are involved. In terms of MCA [6] this obviously corresponds to the projection of the generalized forces only onto the bilinear variables: product of test chain density and matrix density.

To handle with the action in the GF of the test chain we used the Hartree-type approximation (i.e., equivalent to the Feynman variational principle) [8,9,13], which is reasonable when the fluctuations of the test chain are Gaussian. In the case of a polymer melt (high density) this is indeed the case due to the screening effects for the excluded volume [1].

The use of the Hartree-type makes the problem that we deal with analytically amenable and results in the GRE's for the case when the FDT holds as well as for the case when FDT does not hold. In this paper we have restricted ourselves to the first case and have shown that the interaction with the matrix renormalizes not only the friction coefficient (which makes the chain non-Markovian) but also the elastic modulus (which changes the static correlator). The form of the static correlator for the Rouse mode variables is qualitatively supported by MD-simulations [15].

As regards the dynamical behaviour, we have shown that the test chain in a glassy matrix (with the matrix glass transition temperature T_G) undergoes the ergodicity breaking transition at a temperature $T_c(p) \leq T_G$. The critical temperature $T_c(p)$ could be parametrized with the Rouse mode index p and is a decreasing function of p .

We have considered only the A-type transition which is assured by the bilinear term in the expansion of eq. (42). It seems reasonable that keeping the whole exponential function in eq. (42) might lead to a B-type transition also. The results also essentially would change if the off-diagonal elements in the matrix (36) can not be neglected (see eq. (48)). In this case only one ideal transition temperature T_c would be possible. The general theory of a A-type transition was discussed in [23].

This picture of freezing here should not be mixed with a different one, the un-

derlying glass transition by itself (e.g. the glass transition of the matrix at $T = T_G$). According to the present view of this phenomenon [3], the spontaneous arrest of the density fluctuations is driven by those of the microscopic lengthscale k_0 , where k_0 is the wave vector which corresponds to the structure factor's main maximum. The freezing of these fluctuations then arrests the others through the mode coupling.

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APPENDIX A: RESPONSE FIELD DENSITY CORRELATOR

It is more convenient to handle with the spacial Fourier transformation of this correlator

$$\begin{aligned}
& \langle \Pi_l(\mathbf{k}, t) \Pi_j(-\mathbf{k}, 0) \rangle_1 \tag{A1} \\
&= \sum_{(p,m=1)}^M \int ds ds' \langle i\hat{r}_l^{(p)}(s, t) i\hat{r}_j^{(m)}(s', 0) \exp \left\{ i\mathbf{k} \left[\mathbf{r}^{(p)}(s, t) - \mathbf{r}^{(m)}(s', 0) \right] \right\} \rangle_1 \\
&= \sum_{a,b=0}^{\infty} \frac{1}{a!b!} \sum_{p,m=1}^M \int ds ds' \langle i\hat{r}_l^{(p)}(s, t) i\hat{r}_j^{(m)}(s', 0) [i\mathbf{k}\mathbf{r}^{(p)}(s, t)]^a [-i\mathbf{k}\mathbf{r}^{(m)}(s', 0)]^b \rangle_1
\end{aligned}$$

Such multi-point cumulant response functions (MRF) were considered in [12]. The causality condition for these functions asserts that the time argument of at least one \mathbf{r} -variable should be the latest one, otherwise this MRF equals zero. Because of the

same reason self-loops of response functions vanish [10,11]. MRF's which consists only of \hat{r} -variables also vanish.

In the case (A1) all time arguments of the \mathbf{r} -variables are equal to the corresponding time arguments of \hat{r} -variables and as a result the MRF in eq. (A1) vanishes.

APPENDIX B: DERIVATION OF THE HARTREE-TYPE GF

In order to calculate the bilinear Hartree action, we follow the way mentioned in sec.II.B. With these strategy in mind the 2-nd term in the exponent (12) is evaluated as

$$\begin{aligned}
& \frac{1}{2} \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' i \hat{R}_j(s, t) R_j(s', t') I_1(s, s'; t, t') S(\mathbf{k}; t, t') \\
& + \frac{1}{2} \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' i \hat{R}_j(s', t') R_j(s, t) I_2(s, s'; t, t') S(\mathbf{k}; t, t') \\
& + \frac{1}{2} \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' i \hat{R}_j(s, t) R_j(s, t) I_3(s, s'; t, t') S(\mathbf{k}; t, t') \\
& + \frac{1}{2} \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' i \hat{R}_j(s', t') R_j(s', t') I_4(s, s'; t, t') S(\mathbf{k}; t, t') \\
& + \frac{1}{2} \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' i \hat{R}_j(s, t) \hat{R}_j(s', t') I_5(s, s'; t, t') S(\mathbf{k}; t, t') \\
& + \frac{1}{2} \int_0^N ds ds' \int_{-\infty}^{\infty} dt dt' i R_j(s, t) R_j(s', t') I_6(s, s'; t, t') S(\mathbf{k}; t, t') \tag{B1}
\end{aligned}$$

where

$$\begin{aligned}
I_1(s, s'; t, t') & \equiv \left\langle \frac{\delta}{\delta R_j(s', t')} \int \frac{d^3 k}{(2\pi)^3} k_j k_l |V(k)|^2 \exp \{i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')]\} i \hat{R}_l(s', t') \right\rangle \\
I_2(s, s'; t, t') & \equiv \left\langle \frac{\delta}{\delta R_j(s, t)} \int \frac{d^3 k}{(2\pi)^3} k_j k_l |V(k)|^2 \exp \{i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')]\} i \hat{R}_l(s, t) \right\rangle \\
I_3(s, s'; t, t') & \equiv \left\langle \frac{\delta}{\delta R_j(s, t)} \int \frac{d^3 k}{(2\pi)^3} k_j k_l |V(k)|^2 \exp \{i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')]\} i \hat{R}_l(s', t') \right\rangle \\
I_4(s, s'; t, t') & \equiv \left\langle \frac{\delta}{\delta R_j(s', t')} \int \frac{d^3 k}{(2\pi)^3} k_j k_l |V(k)|^2 \exp \{i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')]\} i \hat{R}_l(s, t) \right\rangle \\
I_5(s, s'; t, t') & \equiv \left\langle \int \frac{d^3 k}{(2\pi)^3} k_j k_j |V(k)|^2 \exp \{i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')]\} \right\rangle
\end{aligned}$$

$$I_6(s, s'; t, t') \equiv \left\langle i\hat{R}_j(s, t)i\hat{R}_l(s, t)\frac{\delta^2}{\delta R_n(s, t)\delta R_n(s', t')} \right. \\ \left. \times \int \frac{d^3k}{(2\pi)^3} k_j k_l |V(k)|^2 \exp \{i\mathbf{k} [\mathbf{R}(s, t) - \mathbf{R}(s', t')]\} \right\rangle. \quad (\text{B2})$$

The pointed brackets in eq. (B2) represent the selfconsistent averaging with the Gaussian Hartree action. Taking this into account and using the generalized Wick theorem [22], after straightforward algebra, we have

$$\begin{aligned} I_1(s, s'; t, t') &= \frac{1}{3}G(s, s'; t, t') \int \frac{d^3k}{(2\pi)^3} k^4 |V(k)|^2 \exp \left\{ -\frac{k^2}{3}Q(s, s'; t, t') \right\} & t > t' \\ I_2(s, s'; t, t') &= \frac{1}{3}G(s, s'; t', t) \int \frac{d^3k}{(2\pi)^3} k^4 |V(k)|^2 \exp \left\{ -\frac{k^2}{3}Q(s, s'; t, t') \right\} & t' > t \\ I_3(s, s'; t, t') &= -\frac{1}{3}G(s, s'; t, t') \int \frac{d^3k}{(2\pi)^3} k^4 |V(k)|^2 \exp \left\{ -\frac{k^2}{3}Q(s, s'; t, t') \right\} & t > t' \\ &= -I_1(s, s'; t, t') \\ I_4(s, s'; t, t') &= -\frac{1}{3}G(s, s'; t', t) \int \frac{d^3k}{(2\pi)^3} k^4 |V(k)|^2 \exp \left\{ -\frac{k^2}{3}Q(s, s'; t, t') \right\} & t' > t \\ &= -I_2(s, s'; t, t') \\ I_5(s, s'; t, t') &= \int \frac{d^3k}{(2\pi)^3} k^4 |V(k)|^2 \exp \left\{ -\frac{k^2}{3}Q(s, s'; t, t') \right\} \\ I_6(s, s'; t, t') &= 0 \end{aligned} \quad (\text{B3})$$

where the last equation comes from the fact that the response function $G(t, t') \propto \Theta(t - t')$ and $G(t', t) \propto \Theta(t' - t)$.

The 3-rd term in the exponent eq. (12) can be handled in the same way. The response function for the isotropic matrix has the form

$$P_j(\mathbf{k}, t) = -\frac{ik_j}{k^2}P(\mathbf{k}, t) \quad (\text{B4})$$

where $P(\mathbf{k}, t)$ is the longitudinal part of the matrix response function. Then the Hartree approximation of the 3-rd term in the exponent (12) takes the form

$$\int_0^N ds ds' \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' \left\{ i\hat{R}_j(s, t)R_j(s', t')J_1(s, s'; t, t') + i\hat{R}_j(s, t)R_j(s, t)J_2(s, s'; t, t') \right\}$$

where

$$\begin{aligned}
J_1(s, s'; t, t') &= - \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 P(\mathbf{k}; t, t') \exp \left\{ -\frac{k^2}{3} Q(s, s'; t, t') \right\} \\
J_2(s, s'; t, t') &= \int \frac{d^3 k}{(2\pi)^3} k^2 |V(k)|^2 P(\mathbf{k}; t, t') \exp \left\{ -\frac{k^2}{3} Q(s, s'; t, t') \right\} \\
&= -J_1(s, s'; t, t')
\end{aligned} \tag{B5}$$

Taking into account eq. (B1) with eq. (B2) and eq. (B5) leads to the Hartree-type approximation (15).

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FIGURES

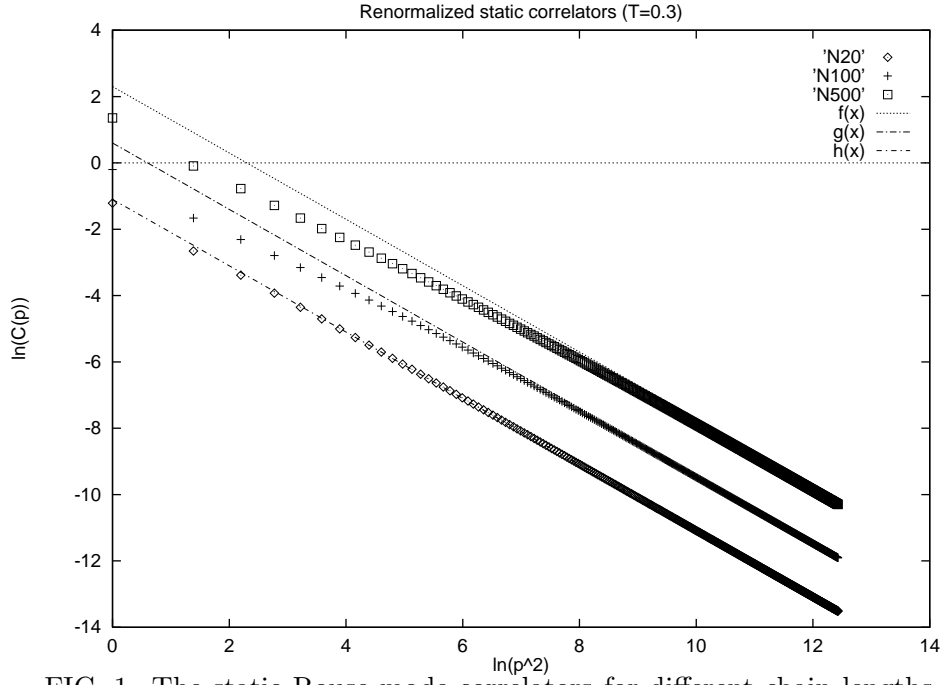


FIG. 1. The static Rouse mode correlators for different chain lengths. The lines represents the simple Rouse case. The temperatures are measured in units of the interaction potential with $\gamma = \sigma = 1$.

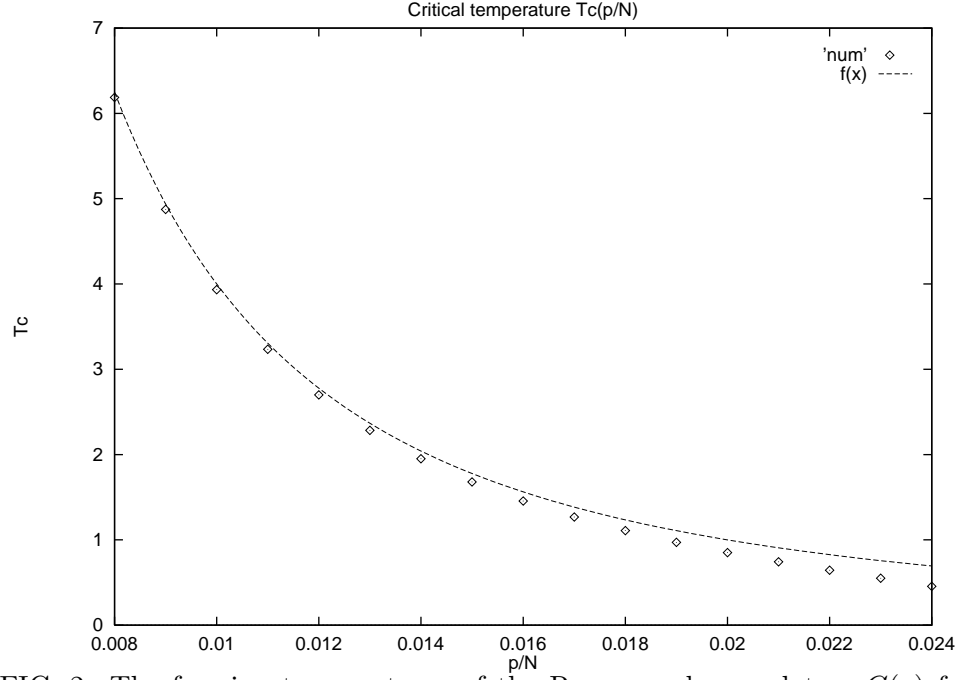


FIG. 2. The freezing temperatures of the Rouse mode correlators $C(p)$ for different wavevectors p/N , where the temperatures are measured in units of the interaction potential with $\gamma = \sigma = 1$. The dashed line represents the freezing temperatures, when only the entropic contributions to the elastic susceptibility are taken into account.

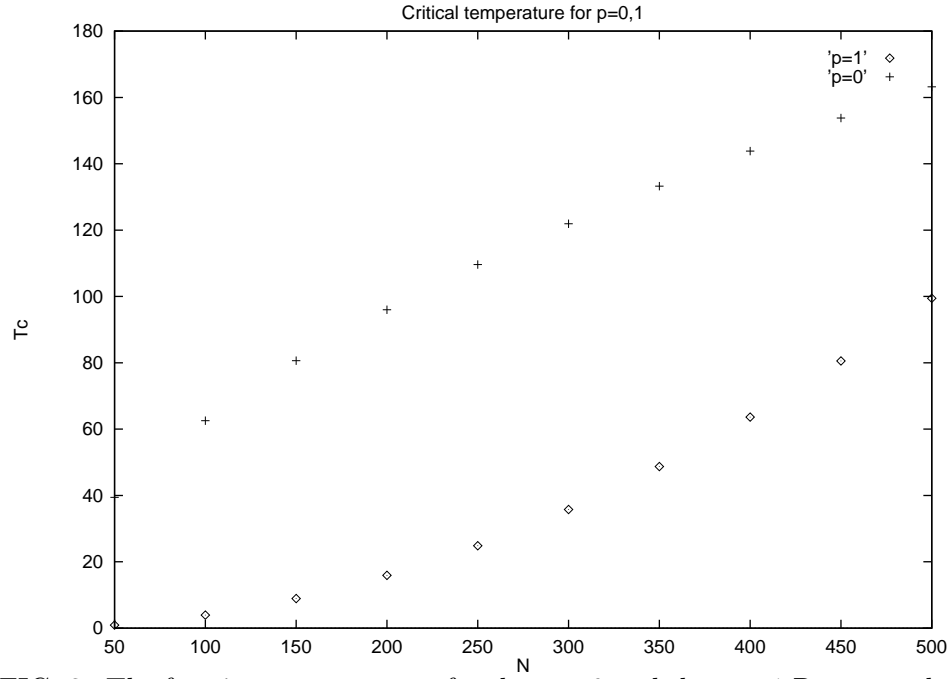


FIG. 3. The freezing temperatures for the $p = 0$ and the $p = 1$ Rouse mode correlators

$C(p)$ of the test chain.